

THERMOPLASTIC POLYESTER COMPOSITIONS HAVING IMPROVED IMPACT PROPERTIES

5 [Field of the invention]

The present invention relates to thermoplastic polyesters having improved impact properties and to impact-modifier compositions.

10 Thermoplastic polyesters, such as PBT (polybutylene terephthalate) and PET (polyethylene terephthalate) possess excellent dimensional-stability, heat-resistance and chemical-resistance properties and are used in the electrical, electronic and motor-vehicle fields. However, at high temperature, during conversion operations, a reduction in the molecular weight of the polymer may occur, leading to a reduction in the impact
15 properties. In addition, polyesters have poor fracture-resistance properties in the case of notched components.

20 The present invention provides thermoplastic polymers in which an impact-modifier composition is added in order to obtain improved impact properties, especially low-temperature toughness. The present invention also relates to this impact-modifier composition that is added to the polyesters to improve the impact properties thereof. These modifier compositions make it possible to achieve impact properties superior to those obtained with each of the compounds separately.

25 [Prior art]

30 Patent US 4,753,890 (= EP 174,343) describes polyesters, such as, for example, polyethylene terephthalate (PET) or polybutylene terephthalate (PBT), which are modified by ethylene-alkyl (meth)acrylate-glycidyl (meth)acrylate copolymers.

Patent US 5,369,154 describes PET/polycarbonate blends containing four different modifiers: a copolymer comprising an epoxide, a copolymer of the core-shell type, an SBR- or SBS- or EPR-type elastomer and a copolymer

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of the SAN or ABS type. These core-shell copolymers comprise fine particles having an elastomer core and a thermoplastic shell.

Patent EP 115,015 describes PET or PBT containing linear low-density polyethylene (LLDPE), glass fibres and optionally a core-shell copolymer.

Patent EP 133,993 describes PET containing a core-shell copolymer and a copolymer of ethylene with either an alkyl acrylate or (meth)acrylic acid.

Japanese Patent Application JP 01,247,454 A, published on 3 October 1989 describes PBT containing an ethylene-alkyl (meth)acrylate copolymer and an ethylene-glycidyl methacrylate copolymer.

Patents EP 838,501 and EP 511,475 describe compositions similar to those of the above Japanese application.

Patent EP 803,537 describes PET and polycarbonate containing a copolymer comprising glycidyl methacrylate. Firstly, the polycarbonate and the copolymer comprising glycidyl methacrylate are blended together and then this blend is incorporated into the PET.

Patent EP 187,650 describes PET containing a core-shell copolymer and a copolymer of ethylene with either maleic anhydride or a (meth)acrylic acid.

Patent EP 737,715 describes PBTs modified by an impact modifier consisting of an ethylene-methyl methacrylate-glycidyl methacrylate copolymer/core-shell copolymer blend. The amount of impact modifier is from 5 to 20 parts per 100 parts of polyester, i.e. 4.8 to 16.7% for 95.2 to 83.7% of polyester, respectively. The proportions of the glycidyl methacrylate copolymer to the core-shell copolymer are in the ratio 15/85 to 20/80. In the examples, the amount of impact modifier is from 18 parts per 100 parts of polyester, i.e. 15.3%, and the proportion of glycidyl methacrylate copolymer to the core-shell copolymer is in the ratio 3/15, i.e. 17/83.

Patent EP 531,008 describes spent (recycled) PBT/polycarbonate (PC) blends containing core-shell copolymers, to which functionalized copolymers are added in order to make them into a new thermoplastic.

These functionalized copolymers are either ethylene-glycidyl methacrylate (GMA) copolymers or ethylene-vinyl acetate-glycidyl methacrylate copolymers. The description quotes proportions of 1 to 97% of polycarbonate, from 1 to 97% of PBT, 1 to 40% of core-shell copolymer and 1 to 40% of glycidyl methacrylate copolymer. In fact, the PBT/polycarbonate blends that it is desired to recycle contain, according to the examples, 15% of core-shell copolymer, which corresponds to more realistic values. Blends (i) of 80 parts of recycled material with 20 parts of glycidyl methacrylate copolymer and blends (ii) of 90 parts of recycled material with 10 parts of glycidyl methacrylate copolymer are then made. The proportions are in the EP 531,008 table below, in which the parts are by weight:

EP 531,008 TABLE

	Compositions such that the core-shell copolymer/PC+PBT ratio = 15/85		
PC+PBT	85	68	76.5
Core-shell copolymer (CS)	15	12	13.5
GMA copolymer		20	10
PC+PBT+CS+ GMA copolymer	100	100	100
GMA/CS copolymer		20/12 = (62/38)	10/13.5 = (43/57)
Proportion of modifier (Core-shell copolymer + GMA copolymer) in PC+PBT		20+12=32%	10+13.5=23.5%

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~~[The technical problem]~~

It has been seen from the prior art that saturated polyesters can have their impact properties improved by the addition of a core-shell copolymer. These polymers have a particularly well defined structure in which the core consists of a polymer having an elastomeric character and the shell has a thermoplastic character. It has also been seen that the improvement in impact strength may be obtained by also incorporating a dispersed phase of an impact modifier optionally containing reactive

functional groups capable of reacting with the functional groups of the polyesters. This reactivity makes it possible to ensure a fine and homogeneous dispersion of the modifier as well as good adhesion. The core-shell copolymer may itself also be functionalized in order to allow better adhesion to the matrix. However, this reactivity is sometimes high and may lead to a reduction in the melt flow index. This reduction in the melt flow index is prejudicial to the injection moulding of large parts or of fine parts.

It has now been found that it is possible to improve the impact properties of thermoplastic polyesters containing essentially no polycarbonate by adding to them two kinds of modifier, namely (a) a core-shell copolymer and (b) either an ethylene-unsaturated epoxide copolymer or an ethylene-carboxylic acid anhydride copolymer or a blend of them but in proportions in the polyester and in (b)/(a) ratios different from those of the prior art EP 737,715. Better impact strength is obtained while maintaining and even improving the melt flow index. It has also been discovered that the impact strength can be improved even more by adding polycarbonate to thermoplastic polyesters containing (a) and (b) in proportions (b)/(a) different from those of the prior art EP 531,008 and lying between 90/10 and 70/30.

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[Brief description of the invention]

The present invention relates to thermoplastic polyester compositions not comprising polycarbonate, which comprise, by weight:

- (i) a thermoplastic polyester;
- (ii) an impact modifier comprising:
 - (a) a core-shell copolymer (A),
 - (b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1), ethylene-unsaturated epoxide copolymers (B2) and blends thereof;
- (iii) the (B)/(A) ratio being between 90/10 and 25/75 for proportions of impact modifier between 2 and 40% in 98 to 60% of polyester, respectively,

and advantageously between 5 and 40% in 95 to 60% of polyester, respectively;

(iv) the (B)/(A) ratio being between 25/75 and 10/90 for proportions of impact modifier between 18 and 40% in 82 to 60% of polyester,

5 respectively.

The present invention also relates to thermoplastic polyester compositions comprising, by weight, the total being 100%:

(i) 98 to 60%, preferably 95 to 60%, of a thermoplastic polyester;

(ii) 2 to 40%, preferably 5 to 40%, of an impact modifier comprising:

10 (a) a core-shell copolymer (A),

(b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1), ethylene-unsaturated epoxide copolymers (B2) and blends thereof;

(iii) the (B)/(A) ratio being between 90/10 and 70/30;

15 (iv) these compositions comprising up to 30 parts of polycarbonate per 100 parts of polyester.

The present invention also relates to an impact-modifier composition which can be added to the thermoplastic polyesters to improve their impact properties and which comprise:

20 (a) a core-shell copolymer (A);

(b) an ethylene copolymer (B) chosen from ethylene-unsaturated carboxylic acid anhydride copolymers (B1), ethylene-unsaturated epoxide copolymers (B2) and blends thereof;

25 • the (B)/(A) ratio being between 90/10 and 25/75 for proportions of impact modifier between 2 and 40% in 98 to 60% of polyester, respectively, and advantageously between 5 and 40% in 95 to 60% of polyester, respectively;

30 • the (B)/(A) ratio being between 25/75 and 10/90 for proportions of impact modifier between 18 and 40% in 82 to 60% of polyester, respectively.

The term "thermoplastic polyester" denotes polymers which are saturated products coming from the condensation of glycols and of dicarboxylic acids, or of their derivatives. Preferably, they comprise the products of the condensation of aromatic dicarboxylic acids having from 8 to 14 carbon atoms and of at least one glycol chosen from the group consisting of neopentyl glycol, cyclohexanedimethanol and aliphatic glycols of formula $\text{HO}(\text{CH}_2)_n\text{OH}$ in which n is an integer ranging from 2 to 10. Up to 50 mol% of the aromatic dicarboxylic acid may be replaced with at least one other aromatic dicarboxylic acid having from 8 to 14 carbon atoms, and/or up to 20 mol% may be replaced with an aliphatic dicarboxylic acid having from 2 to 12 carbon atoms.

The preferred polyesters are polyethylene terephthalate (PET), poly(1,4-butylene) terephthalate (PBT), 1,4-cyclohexylene dimethylene terephthalate/isophthalate) and other esters derived from aromatic dicarboxylic acids such as isophthalic acid, dibenzoic acid, naphthalene dicarboxylic acid, 4,4'-diphenylenedicarboxylic acid, bis(p-carboxyphenyl)methane acid, ethylene bis(p-benzoic) acid, 1,4-tetramethylene bis(p-oxybenzoic) acid, ethylene bis(para-oxybenzoic) acid, 1,3-trimethylene bis(p-oxybenzoic) acid, and glycols such as ethylene glycol, 1,3-trimethylene glycol, 1,4-tetramethylene glycol, 1,6-hexamethylene glycol, 1,3-propylene glycol, 1,8-octamethylene glycol and 1,10-decamethylene glycol. The MFI of these polyesters, measured at 250°C and with 2.16 kg, may vary from 2 to 100 and advantageously from 10 to 80. "MFI" denotes the melt flow index.

It would not be outside the scope of the invention if the polyesters consisted of several diacids and/or several diols. It is also possible to use a blend of various polyesters.

It would not be outside the scope of the invention if the polyesters contained copolyetheresters. These copolyetheresters are copolymers containing polyester blocks and polyether blocks having polyether units derived from polyetherdiols such as polyethylene glycol (PEG), polypropylene glycol (PPG) or polytetramethylene glycol (PTMG),

anhydride with an unsaturated carboxylic acid such as, for example, (meth)acrylic acid.

With regard to the polyethylenes onto which the unsaturated carboxylic acid anhydride is grafted, the term "polyethylene" should be understood to mean homopolymers or copolymers.

By way of comonomers, mention may be made of:

- alpha-olefins, advantageously those having from 3 to 30 carbon atoms; by way of examples of alpha-olefins, mention may be made of propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1—eicocene, 1-dococene, 1-tetracocene, 1-hexacocene, 1—octacocene and 1-triacontene; these alpha-olefins may be used separately or as a mixture of two or more of them;
- esters of unsaturated carboxylic acids, such as, for example, alkyl (meth)acrylates, the alkyls possibly having up to 24 carbon atoms; examples of alkyl acrylates or methacrylates are especially methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate;
- vinyl esters of saturated carboxylic acids, such as, for example, vinyl acetate or vinyl propionate;
- dienes such as, for example, 1,4-hexadiene.

The polyethylene may include several of the above comonomers.

Advantageously, the polyethylene, which may be a blend of several polymers, comprises at least 50 mol% and preferably 75 mol% of ethylene and its density may be between 0.86 and 0.98 g/cm³. The MFI (Melt Flow Index at 190°C/2.16 kg) is advantageously between 0.1 and 1000 g/10 min.

By way of example of polyethylenes, mention may be made of:

- low-density polyethylene (LDPE)
- high-density polyethylene (HDPE)
- linear low-density polyethylene (LLDPE)
- very low-density polyethylene (VLDPE)

The copolymer (B1) is commercially available, produced by radical polymerization at a pressure which may range between 200 and 2500 bar and is sold in the form of granules.

With regard to the ethylene-unsaturated epoxide copolymers (B2), these may be obtained by the copolymerization of ethylene with an unsaturated epoxide or by grafting the unsaturated epoxide to the polyethylene. The grafting may be carried out in the solvent phase or onto the polyethylene in the melt in the presence of a peroxide. These grafting techniques are known per se. With regard to the copolymerization of ethylene with an unsaturated epoxide, it is possible to use so-called radical polymerization processes usually operating at pressures between 200 et 2500 bar.

By way of example of unsaturated epoxides, mention may be made of:

- aliphatic glycidyl esters and ethers, such as allyl glycidyl ether, vinyl glycidyl ether, glycidyl maleate, glycidyl itaconate, glycidyl acrylate and glycidyl methacrylate; and
- alicyclic glycidyl esters and ethers, such as 2-cyclohex-1-ene glycidyl ether, diglycidyl cyclohexene-4-5-dicarboxylate, glycidyl cyclohexene-4-carboxylate, glycidyl 2-methyl-5-norbornene-2-carboxylate and diglycidyl *endo-cis*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate.

With regard to grafting, the copolymer is obtained by grafting an ethylene homopolymer or copolymer as described in the case of (B1), except that an epoxide is grafted instead of an anhydride. With regard to copolymerization, this is also similar to (B1) except that an epoxide is used; it may also have other comonomers, as in the case of (B1).

The product (B2) is advantageously an ethylene-alkyl (meth)acrylate-unsaturated epoxide copolymer or an ethylene-unsaturated epoxide copolymer. Advantageously, it may contain up to 40%, preferably 5 to 40%, by weight of alkyl (meth)acrylate and up to 10%, preferably 0.1 to 8%, by weight of unsaturated epoxide.

Advantageously, the epoxide is glycidyl (meth)acrylate.

Advantageously, the alkyl (meth)acrylate is chosen from methyl (meth)acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and

in which R_2 et R_3 are divalent monocyclic aromatic radicals and Y is a linking radical in which one or two atoms separate R_2 and R_3 . The free valences are generally in the meta or para position with respect to Y. R_2 and R_3 may be substituted or unsubstituted phenylenes; as substituents, mention may be made of alkyl, alkenyl, halogen, nitro and alkoxy. Preferably, the phenylenes are unsubstituted; they may be together or separately meta or para and are preferably para. The linking radical Y is preferably such that one atom separates R_2 from R_3 and is preferably a hydrocarbon radical such as methylene, cyclohexylmethylene, 2-[2.2.1]bicycloheptylmethylene, ethylene, 2,2-propylene, 1,1-(2,2-dimethylpropylene), 1,1-cyclohexylene, 1,1-cyclopentadecylene, cyclododecylene, carbonyl, the oxy radical, the thio radical and sulfone. Preferably, R_1 is 2,2-bis(4-phenylene)propane which comes from bisphenol A, that is to say Y is isopropylidene and R_2 and R_3 are each p-phenylene. Advantageously, the intrinsic viscosity of the polycarbonate, measured in methylene chloride at 25°C, is between 0.3 and 1 dl/g.

The proportion of polycarbonate may represent up to 30 parts per 100 parts of thermoplastic polyester and advantageously from 2 to 20 parts.

Advantageously, the thermoplastic polyester compositions of the invention comprise, per 100 parts by weight, 75 to 95 parts of polyester for 25 to 5 parts of impact modifier, respectively.

The invention also relates to an impact-modifier composition comprising (A) and (B) which can be added to the thermoplastic polyesters to improve their impact properties. In this impact-modifier composition, the proportions of (A) and (B) were defined above.

The thermoplastic polyesters of the invention may also include, in addition to the impact modifier, slip agents, antiblocking agents, antioxidants, UV stabilizers and fillers. The fillers may be glass fibres, fire retardants, talc or chalk.

The thermoplastic polyester/impact-modifier blends are prepared by the usual techniques for thermoplastic polymers in single-screw or twin-

screw extruders, mixers or apparatuses of the BUSS® Ko-kneader type. The polyester and the constituents of the impact modifier, namely the copolymers (A), (B) and (C), may be introduced separately into the blending device. The constituents of the impact modifier may also be added
 5 in the form of a blend prepared in advance, possibly in the form of a masterbatch in the polyester. The additives may be added into these apparatuses, such as the slip agents, the antiblocking agents, the antioxidants, the UV stabilizers and the fillers, whether as they are or in the form of a masterbatch in the polyester or else in the form of a masterbatch
 10 with one or more of the copolymers (A) to (C). The impact-modifier composition comprising (A) to (C) which may be added to the polyesters is also prepared by the previous usual technique of blending thermoplastic polymers.

15 [Examples]

The following products were used:

AX 8900: ethylene-methyl acrylate-glycidyl methacrylate (GMA) copolymer comprising, by weight, 25% acrylate and 8% GMA, having an MFI of 6
 20 (190°C/2.16 kg). It is sold under the brand name LOTADER® par Elf Atochem;

AX 8930: ethylene-methyl acrylate-glycidyl methacrylate (GMA) copolymer comprising, by weight, 25% acrylate and 3% GMA, having an MFI of 6
 25 Atochem;

E920: MBS-type core-shell copolymer with a core essentially based on butadiene-styrene and a shell of PMMA, sold by Elf Atochem under the brand name METABLEND®;

EXL 2314: epoxy-functionalized acrylic core-shell copolymer sold by Röhm
 30 and Haas under the brand name PARALOID®;

PBT: polybutylene terephthalate having an MFI of 20 (250°C/2.16 kg) sold by BASF under the brand name ULTRADUR® B4500.

All the examples were produced with compositions comprising 80% by weight of PBT and 20% by weight of impact modifier. The notched Charpy impact strength complies with the ISO 179:93 standard; the higher the value the better the impact strength.

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FIGURE 1 shows the notched Charpy impact strength at -40°C for PBT containing impact modifier consisting either of AX or of core-shell copolymer or of their blends. Two kinds of AX: AX 8900 and AX 8930 and two kinds of core-shell copolymer: EXL 2314 and E920 were used.

FIGURE 2 shows the impact strengths of these same compositions at $+23^{\circ}\text{C}$. In these figures and in the tables, the epoxide copolymer has been denoted by AX and the core-shell copolymer by CS. The AX/CS ratio is the weight ratio, "30/70" meaning 30 parts of AX to 70 parts of CS. The values are also given in **TABLE 1** and **TABLE 2**.

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TABLE 1

PBT+20%(AX+CS) AX=AX 8900 or AX 8930 CS=EXL 2314 or E920	Notched Charpy impact strength at -40°C			
	AX 8900 EXL 2314	AX 8900/E920	AX 8930 EXL 2314	AX 8930/E920
100/0 AX/CS (comparative)	6.2	6.2	5	5
70/30 AX/CS	9.8	10	8.8	9.9
30/70 AX/CS	7.8	14.75	7.1	9.8
20/80 AX/CS	9.2	10.25		
10/90 AX/CS		13.8		
0/100 AX/CS (comparative)	6.75	8.2	6.75	8.2

TABLE 2

PBT+20%(AX+CS) AX=AX 8900 or AX 8930 CS=EXL 2314 or E920	Notched Charpy impact strength at $+23^{\circ}\text{C}$			
	AX 8900 EXL 2314	AX 8900/E920	AX 8930 EXL 2314	AX 8930/E920
100/0 AX/CS (comparative)	76.4	76.4	55.2	55.2
70/30 AX/CS	99	62.2	67.5	61
30/70 AX/CS	91.8	88.9	82.6	88.4
20/80 AX/CS	87.6	79.5		
10/90 AX/CS		80		

